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TITLE: ⑥ Mechanism of the inhibiting effect of phosphites during the oxidation of paraffinic hydrocarbons.

PERIODICAL: ⑬ Zhurnal fizicheskoy khimii, v. 36, no. 11, 1962, 2537-2539

TOPIC TAGS: inhibiting effect of phosphites, oxidation of hexadecane, mechanism of inhibition, triphenyl phosphite

ABSTRACT: The paper investigates the mechanism of the inhibiting effect of certain phosphites during the thermal oxidation of hexadecane (cetane) which was selected as a model of polyethylene. The basic experiments were conducted with triphenyl phosphite (TPP) the concentration of which varied from 0 to 7%. The oxidation was carried out at 140 to 160°C with forced circulation of oxygen under atmospheric pressure. The content in peroxides was determined by iodometry and that of the consumption of TPP by a method based on its quantitative reaction with butyl peroxide. The results of the study are given in Enclosures 1, 2, 3, and 4. The study established a linear dependence of the induction period on the inhibitor concentration and a correlation between the kinetics of the accumulation of peroxides, the

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consumption of the inhibitor, and the absorption of oxygen. Increase of TPP concentration of 4%. In order to ascertain whether the inhibition of oxidation observed after the termination of the induction period is caused by the hydrolysis product of the phosphite-phenol, formed under the effect of acid oxidation products, an oxidation test was conducted in the presence of 1.2% phenol. It was shown that phenol does not practically affect the duration of the induction period, but considerably lowers the oxidation rate and the amount of absorbed oxygen (Enclosures 1 and 2). Two possible mechanisms of the inhibiting effect of TPP are discussed. The first mechanism, which would involve the decomposition of hydroperoxides formed during the oxidation and reduce the process to an unbranched chain reaction, was rejected on the ground that tributyl phosphite, which is a vigorous reducing agent of hydroperoxides, even in concentrations of 5%, does not increase the induction period, and only slightly lowers the maximum oxidation rate and the consumption of oxygen (Enclosures 1 and 2). A second mechanism, which involves a reaction of phosphites with $RO^{**}2$ and RO radicals and results in the oxidation of phosphite to phosphate by direct attack of P-atoms by oxygen-containing radicals with the formation of the intermediate product $RO^{**}2P(OC^{**}2H^{**}5)_3$, has permitted the explanation of the experimental results of the study and has been adopted by the authors. The considerable inhibiting effects observed after the termination of the induction periods were ascribed to reactions of the unconsumed phosphite and

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its hydrolysis product, phenol, with $RO^{**}2$ radical (Enclosures 1 and 2).

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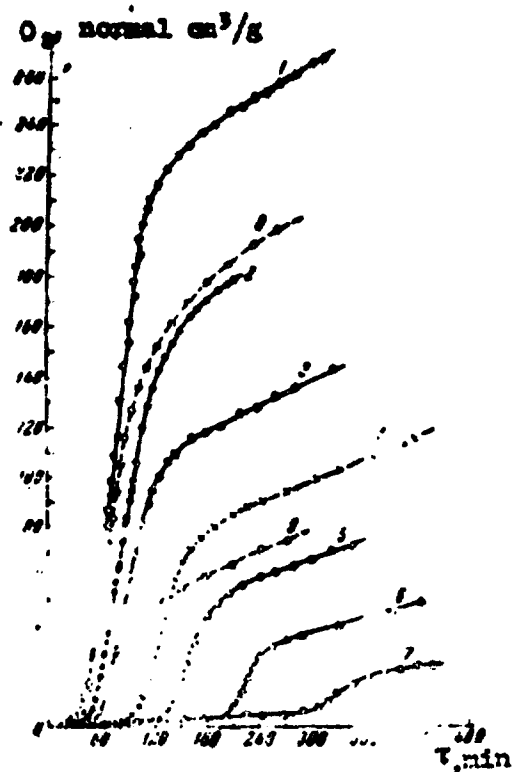
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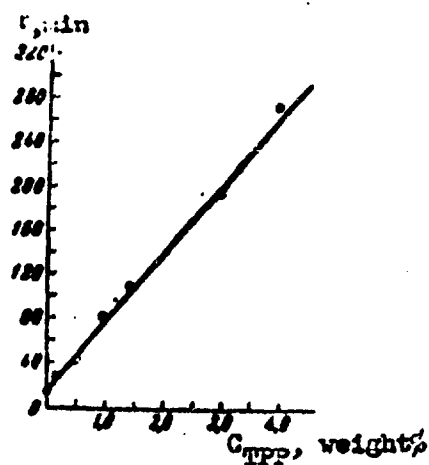
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Kinetics of the absorption of oxygen during the oxidation of cetane at 160°C in the presence of TPP: 1, 0%; 2, 0.1%; 3, 0.5%; 4, 1%; 5, 1.5%; 6, 3%; 7, 4%; 8, in the presence of 5% tributyl phosphite; 9, in the presence of 5% phenol.

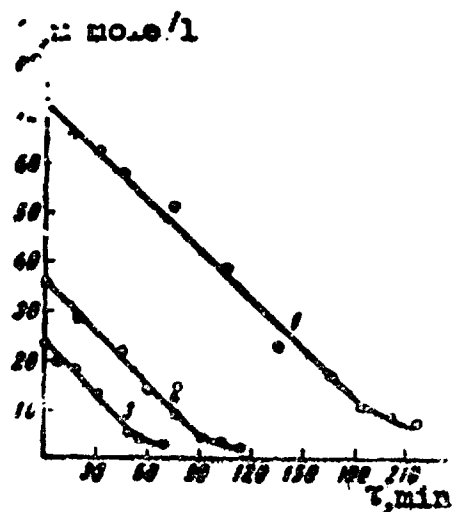


Dependence of the induction period on TPP concentration during the oxidation of cetane (160°C)

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EXPERIMENT NO. A3000131

Enclosure: 4



Kinetics of TPP consumption during the process of inhibited oxidation of cetane (160°C) for various initial inhibitor concentrations:
1, 71.7 mmole/l (3%); 2, 3.58 mmole/l (1.5%); 3, 23.9 mmole/l (1%)